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(54) **Method of coating a continuously moving web**

(57) The invention is directed to a process for coating a continuously moving web, comprising a heat treatment of the surface of the web with infrared radiation, prior or after setting a surface potential on the web with a discharging device, followed by applying at least one

emulsion layer on the web with a coating device wherein the viscosity of the undermost emulsion layer, which comprises a solution at least gelatine, is lower than 40 mPas.

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**Description**

**[0001]** The present invention relates to a method of coating a continuously moving web, which comprises heating the surface of the web and setting a surface potential by a discharging device prior to applying one or more coating solutions (hereinafter referred to as "emulsion"). Said coating methodology is especially suitable for producing photographic materials such as photosensitised material film and photographic print paper at a high speed and with an excellent uniformity of the emulsion thickness.

**Background of the invention**

**[0002]** In most of the industries where coating technology is involved, the speed of coating is regarded as one of the important factors that influences the economical value of the product. The higher the coating speed, the faster the product is produced and thus the more economical the product will be.

**[0003]** It is known in the photographic industry that the speed of the coating process is determined, among others, by the wetting phenomena occurring between the emulsion and the surface of the web. The influences of the rheology and the wetting properties of the emulsion on the coating process is, for example, described in "Liquid Film Coating", edited by Stephan F. Kistler and Peter M. Schweizer, pages 63 to 182. Another example is described in US-A 4572849 where it is suggested to select a low viscosity for the undermost layer in order to improve the wetting of the web and, thus, to increase the coating speed. The lower the viscosity is, the higher the coating speed will be.

**[0004]** At a certain coating speed, wetting will not be the limiting factor anymore for further increase of the speed. There is another phenomena known as "air entrainment", that limits the speed. Herein, the air between the emulsion and the web is entrained during the coating process and can not be dissolved in the emulsion. Consequently a serious coating defect occurs.

**[0005]** In EP-A 0530752 it has been suggested to apply electrostatic charges on the surface of the web in order to prevent the air entrainment and to increase the coating speed significantly. However, the application of the electrostatic charge is limited by the applied voltage. A high voltage, which is needed as the coating speed is increasing, will result in a non-uniform coating thickness that causes a visible quality problem on the photographic product, known as "blur" or "mottle" defect.

**[0006]** In order to solve the blur or mottle problem, heating of the web was suggested. The suggested coating methodology involves thus heating the web, followed by electrostatic charging the web prior to coating the emulsion.

**[0007]** In the method of EP-A 0530752, where the web is heated by means of convection or conduction methodology, an emulsion setting problem has been observed immediately after the coating process when the web temperature is higher than 45°C. The problem occurred at a gelatine concentration of the undermost layer of 6wt% and a viscosity of 40 mPas. The setting problem is a known problem in the coating technology, where the emulsion layers are not transforming to a gel phase during the chilling process. The setting problem is expected to be worse when the viscosity in the undermost layer becomes lower. The higher the viscosity, the better the emulsion setting will be.

**Summary of the invention**

**[0008]** There remains, thus, a need for a high speed coating method comprises of pre-heating and electrostatic charging the web, without having the problem with emulsion setting and non-uniformity of emulsion thickness caused by the non-uniform surface charge on the web.

**[0009]** The object of the present invention is to provide a coating method for fulfilling the need described above that can not be realised by the conventional coating methods.

**[0010]** More specifically, it is an object of the invention to provide a high speed coating method, wherein the viscosity of the undermost emulsion layer is low, without having any emulsion setting problem immediately after the coating process.

**[0011]** Another object of the invention is to provide a coating method wherein an excellent uniformity of emulsion's thickness can be realised and, thus, providing a photographic material which is free from blur or mottle defects.

**[0012]** The foregoing object of the invention has been achieved by the provision of a coating process for coating a continuously moving web, comprising a heat treatment of the surface of the web with infrared radiation, prior or after setting a surface potential on the web with a discharging device, followed by applying at least one emulsion layer on the web with a coating device wherein the viscosity of the undermost emulsion layer, which comprises a solution containing at least gelatine, is lower than 40 mPas (at a shear rate of 50 sec<sup>-1</sup>).

**Detailed description**

**[0013]** The invention resides on the need for an improved product quality, especially the blur or mottle defect and an

increase of the coating speed.

**[0014]** During the experiment, it was confirmed that a low viscosity of the undermost emulsion layer is more effective for increasing the coating speed than a higher one. Reduction of said viscosity from about 40 to 15 mPas resulted in a coating speed increase of about 40%.

**[0015]** Furthermore, the application of electrical charge on the surface of the web between 0.5 to 2.0 kV has additionally increased the coating speed with 20%. So there is a significant increase of the coating speed when the above mentioned conditions are combined. Unfortunately, the blur level of said combination is not satisfying our standard quality target.

**[0016]** It is believed that the application of electrostatic charge on the surface of the web causes a non-uniform surface potential. This non-uniformity results in a thickness variation of the emulsion, which is determining the blur (US-A 5138971). In order to solve this problem, the web is heated prior to coating since the mobility of the ions present at the surface of the web is higher at higher temperature. Consequently, the surface potential of the web will be distributed uniformly and it will improve the blur level of the coated product.

**[0017]** The most serious bottleneck for said method is the emulsion setting problem which will occur especially when the viscosity of the undermost layer is low.

**[0018]** Furthermore, it was also concluded in EP 0530752 that the web temperature has also an important role in the setting process. When the viscosity of the most underlayer is 40 mPas, setting problem will occur at web temperature of 45°C. The higher the web temperature and / or the lower the viscosity of the undermost layer, the sooner the emulsion setting problem will occur. However, in order to achieve a high coating speed, the undermost emulsion layer needs to have a low viscosity.

**[0019]** In this invention, it is surprisingly discovered that the emulsion setting problem will not occur even at a very low viscosity of the undermost emulsion layer, when we heat up the surface of the web by using Infra Red radiation, especially at the wavelength which is defined as the Near Infra Red.

**[0020]** This invention provides thus a high speed coating method that contains a minimum level of the blur quality defect, and that does not result in any form of emulsion setting problem. The invented method comprises heat treatment of the web by using Infra Red radiation, setting a surface potential on the surface of the web by a discharging device before coating the emulsion layers wherein the viscosity of the undermost emulsion layer is lower than 40 mPas.

**[0021]** Without being bound by it, the theory behind the above mentioned effect may perhaps be found in the fact that the Infra Red has a specific physical characteristic to interact with most of the hydroxyl groups which are mainly present on the surface of the web that is undercoated with gelatine. This effect, which is different compared to the conventional method where the whole web is heated, has presumably resulted in heat treatment of the web-surface only. Consequently, a relatively low amount of heat is absorbed by the web, which will not cause emulsion setting problem. At the same time, the high surface temperature will still increase the mobility of the ions at the surface of the web, resulting in a uniform potential distribution.

**[0022]** In this invention, it is discovered that the Infra Red wavelength between 0.78 and 1.5  $\mu\text{m}$ , which is known as the Near Infra Red, has the preference above the midwave or longwave Infra Red region (wave length above 1.5  $\mu\text{m}$  to 1.0mm). By limiting the wavelength to the Near Infra Red region, the said coating method can be applied to a web which has a surface temperature, measured directly after the heat treatment, of up to 120°C without having any emulsion setting problem. At this surface temperature, the surface potential is distributed very uniformly, such that the observed small non-uniformity of the emulsion thickness can only originate from the coating nozzle.

**[0023]** One of the advantage of using the Near Infra Red radiation is that the web temperature can be increased in an extremely short treatment period, usually less than 1 seconds, even at coating speed higher than 250 m/min. Therefore we prefer to apply the Near Infrared device at a radiation temperature above 2500°K, preferably above 3000°K.

**[0024]** The advantage of applying such a high web temperature is that one can use electrodes which are known to cause a poor potential distribution, e.g. needles, brush etc.

**[0025]** The minimum temperature at the surface of the web is 30°C. At temperature lower than 30°C, the mobility of the ions will be very low and no significant blur improvement can be expected.

**[0026]** The preference temperature range for the surface of the web according to the invention is between 35°C and 90°C, and more preferably from above 45°C to 85°C.

**[0027]** There are two alignments of the apparatus which are included in the invention, those are: (1) the surface potential discharging device is located in between the Infra Red radiation device and the coating nozzle, and (2) the Infra red radiation device is located in between the surface potential discharging device and the coating nozzle. The difference between these two alignments lies in the necessity of heating up the surface of the web before or after setting the surface potential on the web by the discharging device. In the case of a web made of a plastic film, it is preferable to heat up the web first before setting the surface potential, since the surface of plastic films is easier to be stretched flat at a high temperature. But in case of resin-coated paper, the surface of the web is already flat even at room temperature. Therefore, charging of surface potential on said paper can be effectively done at low surface temperature whereafter the Infra Red radiation will heat up the web-surface and provide a uniform potential distribution

on the surface of the web.

**[0028]** In this invention, the term "web" is intended to include those of paper, plastic film, resin-coated paper and synthetic paper, wherein an undercoat layer of gelatine is formed on the web.

**[0029]** Examples of the material of the plastic film are polyolefins such as polyethylene and polypropylene, vinyl copolymers such as polyvinyl acetate, polyvinyl chloride and polystyrene, polyamide such as 6,6-nylon and 6-nylon, polyesters such as polyethylene terephthalate, polyethylene-2 and 6-naphthalate and polycarbonate, and cellulose acetates such as cellulose triacetate and cellulose diacetate. The resin employed for manufacturing the resin-coated paper is typically polyolefin, such as polyethylene.

**[0030]** The term "coating solution" or "emulsion" as used herein is intended to include a variety of coating solutions, such as those used to form a photo emulsion layer, undercoat layer, protective layer, and a back layer thereby to form a photographic or photo-sensitive material, or those for forming an adhesive layer or colouring layer. The emulsion or coating solution comprises at least gelatine solution. Examples of the suitable gelatine are pigskin gelatines, bone gelatines, fish gelatines, gelatine produced by biotechnological process, chemically modified gelatines and hydrolysed gelatines.

**[0031]** In applying the emulsion to the web, one may employ a slide coating method, a roller bead coating method, a spray coating method, an extrusion coating method or a curtain coating method.

### Example 1

**[0032]** Several experiments, comparing the invention with the reference, have been done in which a 200  $\mu\text{m}$  thick polymer-laminated paper wherein a gelatine layer was coated on the surface of said paper, was used as a web.

**[0033]** Photo-sensitive layers containing silver-halide, colour filter layers and a protective layer were coated on the web by means of a slide coating method. The total quantity of emulsion solution was 95  $\text{cc}/\text{m}^2$ . The undermost layer, which was a yellow colouring layer, had a gelatine concentration of 3.5~6 wt.%, a viscosity of 15~40 mPas (at a shear rate of 50  $\text{sec}^{-1}$ ) and a flow rate of 10  $\text{cc}/\text{m}^2$ .

**[0034]** The coating was carried out with a coating gap of 200  $\mu\text{m}$  and a coating pressure of about 60 mm  $\text{H}_2\text{O}$  under the atmospheric pressure.

**[0035]** The web was heated with hot air or NIR, and charged by the corona discharge-like electrode. Thereafter the web was coated at a web-temperatures varying between 22 °C to 75°C. In the experiments the critical coating speeds were determined, representing the maximum coating speed where the onset of air entrainment was not observed. The results of the experiments are given in table 1.

Table 1

| Webtemperature, CCS and setting |                |              |              |                  |          |             |
|---------------------------------|----------------|--------------|--------------|------------------|----------|-------------|
| Technology                      | Heating device | [Gelatine] % | Visco [mPas] | Surf. Temp. [°C] | Setting  | CCS [m/sec] |
| Reference                       | Hot air        | 6.0          | 40           | 22               | OK       | 178         |
|                                 |                |              |              | 38               | OK       | 195         |
|                                 |                |              |              | 45               | OK       | 197         |
|                                 |                |              |              | 50               | Not OK*) | No data     |
|                                 | Hot air        | 4.5          | 25           | 45               | Not OK*) | No data     |
| Invention                       | NIR            | 4.5          | 25           | 22               | OK       | 191         |
|                                 |                |              |              | 35               | OK       | 248         |
|                                 |                |              |              | 45               | OK       | 256         |
|                                 |                |              |              | 75               | OK       | 254         |
|                                 |                | 3.5          | 15           | 22               | OK       | 205         |
|                                 |                |              |              | 35               | OK       | 266         |
|                                 |                |              |              | 45               | OK       | 275         |
|                                 |                |              |              | 75               | OK       | 277         |

\*) Critical coating speed can not be determined due to emulsion setting problem

**[0036]** It can be seen that increasing the surface temperature to a value above 45 °C does not have a significant

effect on CCS (Critical Coating Speed). Furthermore the data show that when the NIR heating method is used, even at lower viscosity, above a webtemperature of 45 °C, no setting problem occurs.

[0037] The beneficial effect of higher webtemperatures will be shown in next example.

## Example 2

[0038] Another set of experiments was done, analysing the relation between webtemperature, surface potential and quality (mottle). A 200 µm thick polymer-laminated paper wherein a gelatine layer was coated on the surface of said paper, was used as a web.

[0039] Photo-sensitive layers containing silver-halide, colour filter layers and a protective layer were coated on the web by means of a slide coating method. The total quantity of emulsion solution was 95 cc/m<sup>2</sup>. The undermost layer, which was a yellow colouring layer, had a gelatine concentration of 3.5 wt.%, a viscosity of 15 mPas (at a shear rate of 50 sec<sup>-1</sup>) and a flow rate of 10 cc/m<sup>2</sup>.

[0040] The coating was carried out with a coating gap of 200 µm and a coating pressure of about 60 mm H<sub>2</sub>O under the atmospheric pressure.

[0041] A surface potential was applied to the web by a corona discharge-like electrode. The web was heated by using a Near Infrared (NIR) heating, which has a radiation temperature higher than 2500 K. The desired surface temperature was achieved by adjusting the NIR radiation temperature. The distance between the heater and slide coating device was designed as short as possible in order to keep temperature losses minimal. Thereafter the web was coated at a web-temperature varying between 22 °C to 75°C, while the web-surface potential was varied up to 1.00 kV.

[0042] In the experiments, the surface potential was recorded in machine- and cross web direction. The coating quality was determined by measuring the whiteness parameters -a and -b. The bigger the variation in a and b, the bigger the mottle. Measurements were done using a BARBIERI electronic spectrophotometer model Spectro 100xy.

[0043] The surface potential as well as the temperature of the web surface was measured just before applying the emulsion.

[0044] The results can be obtained from table 2.

Table 2

| Surface potential, CCS and quality |                   |                             |       |      |                    |                                      |     |
|------------------------------------|-------------------|-----------------------------|-------|------|--------------------|--------------------------------------|-----|
| Surf. Temp.                        | Surface potential |                             |       |      | CCS* <sup>1)</sup> | Quality (mottle) by colour whiteness |     |
| [°C]                               | Potential         | Distribution* <sup>2)</sup> | Noise |      | [m/min]            | Variation                            |     |
|                                    | [KV]              | [%]                         | [V]   | [%]  |                    | Δa                                   | Δb  |
| 22                                 | 0.0               | --                          | --    | --   | 209                | 0.3                                  | 0.2 |
| 22                                 | 0.3               | 33                          | 30    | 10.0 | 225                | 0.4                                  | 0.4 |
| 22                                 | 1.0               | 42                          | 70    | 7.0  | 252                | 0.5                                  | 0.7 |
| 35                                 | 1.0               | 20                          | 46    | 4.6  | 305                | 0.4                                  | 0.6 |
| 75                                 | 1.0               | 7                           | 23    | 2.3  | 308                | 0.4                                  | 0.3 |

\*1) No setting problems occurred

\*2) Distribution is meant: (max. potential - min. potential) in cross web direction

[0045] It is known that surface potential variations are responsible for the quality of the coating. It is also known that therefor increasing the potential will decrease the quality.

[0046] The noise and the uniformity of the surface potential are improved significantly by increasing the webtemperature. The improvement in quality is reflected in a reduction of the a- and b-variations.

## Claims

1. A process for coating a continuously moving web, comprising a heat treatment of the surface of the web with infrared radiation, prior or after setting a surface potential on the web with a discharging device, followed by applying at least one emulsion layer on the web with a coating device wherein the viscosity of the undermost emulsion layer, which comprises a solution containing at least gelatine, is lower than 40 mPas.

2. The process according to claim 1 wherein the said viscosity of the undermost emulsion layer is lower than 25 mPas.
3. The process according to claim 1 or 2 wherein the surface of the web is treated with a Near Infra Red radiation.
- 5 4. The process according to claims 1-3 wherein the temperature of the web, directly after the heat treatment, is between 30°C and 120°C.
5. The process according to claim 4 wherein the web-temperature, directly after the heat treatment, is between 35°C and 90°C.
- 10 6. The process according to claim 5 wherein the temperature of the web, directly after the heat treatment, is from above 45°C to 85°C.
- 15 7. The process according to claims 1-6 wherein said discharging device comprises a direct current corona discharge electrode.
8. The process according to claims 1-7 wherein said coating device comprises a slide coating method, a roller bead coating method, a spray coating method, an extrusion coating method or a curtain coating method.
- 20 9. The process according to claims 1-8 wherein said web is a polymer laminated photographic base paper, a synthetic paper or a plastic film wherein a gelatine layer is provided on the web.
- 25 10. The process according to claim 9 wherein said plastic film comprises a polyethylene, polypropylene, polyvinyl acetate, polyvinyl chloride, polystyrene, polyamide, polyethylene terephthalate, polyethylene-2 and 6-naphthalate, polycarbonate, or cellulose acetates.
11. The process according to claims 1-10 wherein the web is provided at least with one layer of a photographic emulsion.
- 30 12. The process according to claims 1-11 wherein said gelatine comprises biotechnologically produced gelatine, pig-skin gelatine, hydrolysed gelatine, fish gelatine, bone gelatine, and chemically modified gelatine.
13. Photographic print paper or photographic negative film obtainable by the process of claims 1-12.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 20 3106

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